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Optical properties of ZnO, $Zn_{0.99}Mn_{0.01}O$ nanopowders

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The photoluminescence and photoluminescence excitation spectra of $Zn_{0.99}Mn_{0.01}O$ nanopowders are presented in this paper. Detected peaks at energies $\hbar\omega$ higher than the energy gap in the photoluminescence excitation spectra allow us to assume that the Zhang-Rice-like states in forbidden gap due to the strong exchange coupling between 3d localized spin and valence band holes are related with valence band states perturbed by strong p-d hybridization.

1 Introduction In last years many researches of dilute magnetic semiconductors (DMS) with the ferromagnetic ordering at T_c>300 K appear. The main interest is centered around the ZnO:3d materials for which the theoretical calculations show us that the increasing of T_c takes place due to the strong hybridization between the 3d localized spin and valence band holes and appearing Zhang-Rice-like (ZR) states [1-3]. It is suggested that these antibonding state is split out from the valence band top deeply into the band gap and the optical transitions from the ZR- state to the conduction band cause very strong light absorption in monocrystals and nanocrystals of $Zn_{1-x}Mn_xO$ in the energy region of 2,2-3.0 eV [4,5]. However in photoluminescence (PL) spectra of colloidal nanocrystals of $Zn_{1-x}Mn_xO$ the ZR-state is not observed [5]. Recently the PL-peak at the energy of 2,9 eV for $Zn_{0.99}Mn_{0.01}O$ nanopowder, prepared by the gas phase synthesis method, was detected [6]. In the 2,9 eV photoluminescence excitation (PLE) spectrum were observed three wide peaks in the region of interband transitions at the energies of 3.9, 4.5 and 5.3 eV. In this paper the researches of the $Zn_{0.99}Mn_{0.01}O$ system were continued in order to understand the reason of appearance of 2.9 peak in PL-spectrum and to compare with the well learned ZnMnS compound. Our results allow us to think that the Mn^{2+} ions in the $Zn_{0.99}Mn_{0.01}O$ nanopowder induce the additional ZR-like state. The optical transitions between this state and the ground state of the crystal create the 2.9 peak in PL-spectrum and the broad peculiarities in the PLE spectrum of this illumination at the energies of 3.9, 4.5 and 5.3 eV in the region of interband transitions.

2 Experimental detail

Nanopowder with the size of the nanocrystals of 30 nm were prepared by the method of the gas phase synthesis [7] annealed in air at 400°C during 1 hour. The manganese concentration in nanocrystals $Zn_{1-x}Mn_xO$ before and after the annealing was determined by inductively–coupled plasma mass spectroscopy (iCAP 6000, Thermo) and x=0.01. Optical spectra in [6] were observed for nanocrystals $Zn_{1-x}Mn_xO$ with x=0.01 also.

3 Results and discussion

Figure 1 presents the PL and PLE- spectra of $Zn_{0.99}Mn_{0.01}O$ nanopowder before and after annealing. In both cases in PL- spectra we can see low energy peaks with the maxima at the energies of 2.1 and 2.3 eV and high energy peak at the energy of 2.9 eV. Low energy peaks were caused by deep defects in the crystals, which had been subjected to the heat treatment in oxygen atmos-

phere [8]. We assume that the quantity of oxygen vacancies decreased in result of the annealing in air. The decreasing of the peak 2.9 eV intensity, which clearly expressed in Fig. 1a, is caused probably by the following fact: this peak is formed by the complex Mn^{2+}-V_O. In PLE spectra of 2.9 eV peak for as grown (i.e. without the annealing) nanopowder three peaks at the energies of 3.9, 4.5 and 5.3 eV are observed [6]. After the annealing the intensity of these peaks decreases, but the increasing of PLE spectrum with the increasing of the light quantum energy is clearly expressed, especially for the last peak 5.3 eV. Such behavior of PLE spectrum is significantly different in its character from that for the luminescence through the deep levels, when the intensity decreases along with the increasing of the excitation energy in the region $\hbar\omega > E_g$ [6].

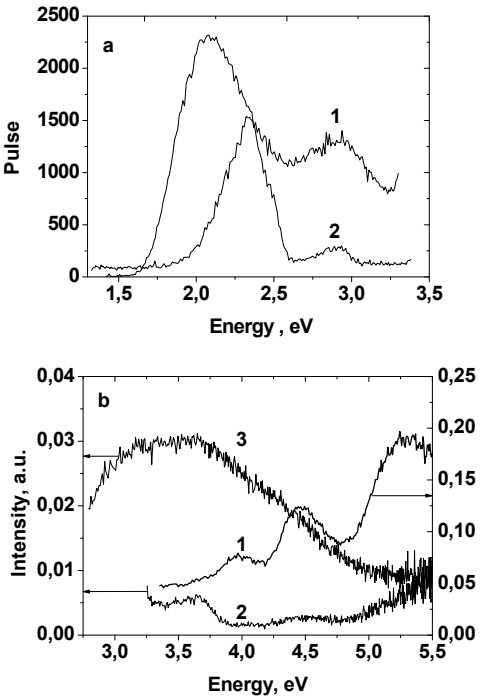

Figure 1 a) PL spectra of as grown $Zn_{0.99}Mn_{0.01}O$ nanocrystals (1) (excitation E =3.64 eV, T = 86 K); and of annealed $Zn_{0.99}Mn_{0.01}O$ nanocrystals (2) (excitation E = 3.718 eV, T = 90 K); b) PLE spectra (peak 2.9 eV) of as grown $Zn_{0.99}Mn_{0.01}O$ nanocrystals, T = 86 K (1); and of the annealed $Zn_{0.99}Mn_{0.01}O$ nanocrystals, T = 90 K (2); PLE spectrum (peak 2.34 eV) of the annealed $Zn_{0.99}Mn_{0.01}O$ nanocrystals, T = 90 K (3).

For comparison we demonstrate the PL and PLE spectra for $Zn_{0.995}Mn_{0.005}S$ (Fig. 2). Luminescence with the energy of 2.12 eV caused by the intracentral transitions of Mn^{2+} ion ($^4T_1$-$^6A_1$). The PLE spectrum exhibits intensive peaks due to the transitions to high-energy states of Mn^{2+} ion ($^4T_2$ and $^4A_2$, ^4E), whereas in the interband transition region we can see the maximum near the E_g and smooth decreasing of intensity at $\hbar\omega > E_g$. Similar decreasing of excitation intensity at $\hbar\omega > E_g$ takes place for the luminescence peaks 2.34 eV (Fig. 1-b3) and 2.12 eV [6] due to the transitions through the deep states.

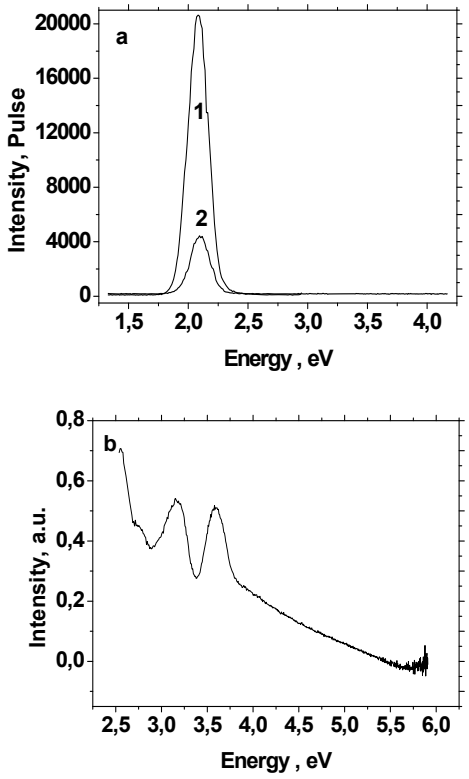

Figure 2 a) PL spectra of the $Zn_{0.995}Mn_{0.005}S$ monocrystal, excitation E = 3,230 eV (1) and 4.78 eV (2); b) PLE spectrum of the $Zn_{0.995}Mn_{0.005}S$ monocrystal, emission E =2,12 eV

We can see that the PLE spectrum for $Zn_{0.99}Mn_{0.01}O$ nanopowders (emission 2.9 eV, Fig. 1) significantly distinguishes from that for luminescence of 2.1 eV of $Zn_{0.995}Mn_{0.005}S$ monocrystals (Fig. 2) and emission 2.34 eV of the $Zn_{0.99}Mn_{0.01}O$ nanocrystals (Fig. 1). On the other hand some resemblance exists. This similarity consists in the fact that the luminescence and its excitation in $Zn_{0.99}Mn_{0.01}O$ and $Zn_{0.995}Mn_{0.005}S$ take place through the series of some states connected with one another. In the case of $Zn_{0.995}Mn_{0.005}S$ it is the intracentral states of Mn^{2+} ion d^5 shell. In the case of $Zn_{0.99}Mn_{0.01}O$ a situation is not so simple. A small band length in $Zn_{1-x}Mn_xO$ results in a strong hybridization between d and p states $Zn_{1-x}Mn_xO$. For this case the ZR-like states due to the strong exchange coupling between 3d localized spin and valence band holes were predicted for description of the intensive absorption band [1]. Really in $Zn_{1-x}Mn_xO$ the ZR-like states are more complicated due to Γ_7, Γ_9 and Γ_7 sub-bands at the valence band top and to possible influence of oxygen vacancies in a Mn^{2+} environment. So, we have some reasons to consider that there is the ZR-like state providing the 2.9 eV lumi-

nescence band. This state is schematically presented on Fig. 3. The transition from this state to the ground state forms the 2.9 eV PL peak. But the excitation of this peak takes place through higher valence band states perturbed by a strong hybridization between d and p states $Zn_{1-x}Mn_xO$. They are denoted as V_1, V_2 and V_3 and displayed at the energies higher than E_g in Fig. 3.

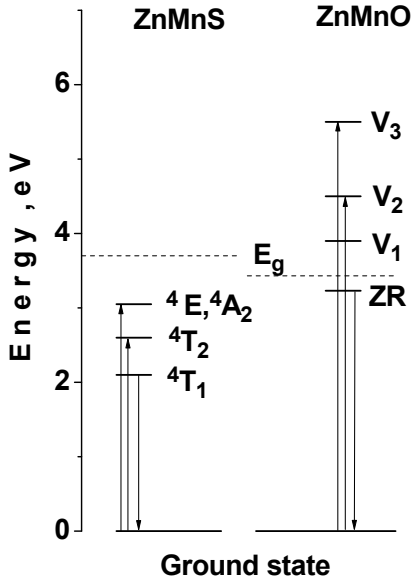

Figure 3 Left panel: schematic presentation of Mn^{2+} energy levels in $Zn_{1-x}Mn_xS$ monocrystal, transition $^4T_1$ -$^6A_1$ forms the 2.1 eV emission and transitions to higher intracentral states which form peaks of PLE spectrum (Fig. 2b); right panel: the $Zn_{1-x}Mn_xO$ Zhang-Rice-like state and valence band V_1, V_2, V_3 states and transitions forming the 2.9 eV PL peak and the V_2 and V_3 PLE peaks are shown.

So we can assume some relation between ZR-like states and V_1, V_2 and V_3 bands.

4 Conclusion In our paper for the first time the experimental PL and PLE spectra are interpreted in terms of the theoretical descriptions of the $Zn_{1-x}Mn_xO$ strong d-p hybridization [1-3]. We think it to be interesting to further investigate these states in the $Zn_{1-x}Mn_xO$ semiconductors in particular to understand better the role of the oxygen vacancies.

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